PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-207123
(43)Date of publication of application : 31.07.2001

(51)Int.Cl. C09D185/00
B05D 5/00
B05D 5/08
C09D 5/00
C09D201/00
C09K 3/18
// C09D133/00
C09D183/02

(21)Application number : 2000-268026
(22)Date of filing : 05.09.2000

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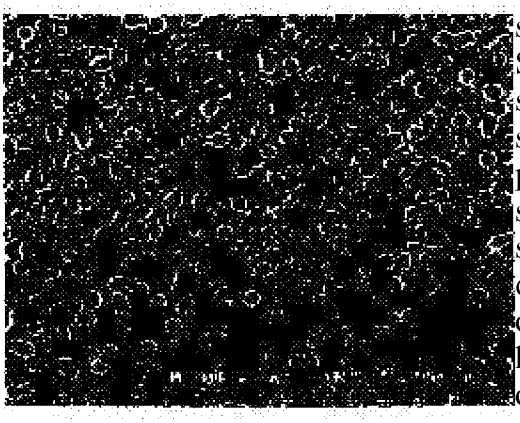
(30)Priority
Priority number : 11326093 Priority date : 16.11.1999 Priority country : JP

(54) FILM HAVING HIGH HARDNESS AND HIGH DROPLET SLIDABILITY AND METHOD FOR PRODUCING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a film structure having both droplet slidability and hardness, to provide a method for producing the same, and to provide a coating material.
SOLUTION: This coating material comprises a solution or emulsion obtained by adding, to a solvent, a metal alkoxide and/or a sol having a primary particle diameter of ≤100 nm and a substance having characteristics which phase-splits from the above components and decomposed, burns or sublimes at a temperature of room temperature to 700°C. The film having high hardness and high droplet slidability is obtained by coating a substrate with the coating material, thermally treating the coated substrate in a temperature range of room temperature to 700°C to form the primary layer having many fine holes having an average hole diameter of 100 nm to 2 μm, and then coating at least one portion of the primary layer with a water-repelling agent.



DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]Structure control is easy for this invention, and it relates to the paint used for a membrane structure object simultaneously provided with the outstanding planing nature and hardness, a manufacturing method for the same, and it.
[0002]
[Description of the Prior Art]Many planing nature surfaces are obtained by processing the surface with silicon, fluoride, etc. conventionally.
In the planing nature surface obtained by such conventional technology, the angle of contact with water of the fall angle of the drop was an about 50-60-degree thing to a 20-mg drop at about 100-110 degrees.
And this processing is already put in practical use to clothing, the glass of a car, a painted surface, etc.
[0003]It is known that the surface which can make the touch area of that surface and water remarkably small and where an angle of contact is provided with not less than 150-degree very high water repellence (super-water repellence) by giving a suitable structure for the low energy surface on the other hand is obtained. And if planing nature with this super-water repellence surface high as it is is shown, a high effect is expectable to various purposes, such as snow-stucking raindrop prevention, preventable contamination, rust prevention, electric insulation, and a mold-release characteristic.
[0004]However, simple correlation is not necessarily between the character of this super-

water repellence, and the character (planing nature) in which waterdrop falls, As for the surface, in order to give high planing nature, it is just insufficient to have super-water repellence (in order to lower resistance with the surface and water even so that waterdrop falls by only several inclination).
[0005]As a result of this invention persons' doing research so that inclination of mere abundance extent may also give planing nature high like waterdrop falls to the surface since it was such, by making the surface of a super-water repellent film into detailed rugged structure, It succeeded in even inclination of about only 1 time obtaining the film (super-water repellent film) which has planing nature high like waterdrop falls (Japanese Patent Application No. No. 294636 [11 to]).
[0006]
[Problem(s) to be Solved by the Invention]However, since it is necessary to form detailed rugged structure in the surface fundamentally in order to obtain such a super-water repellent film, it originates in this, the hardness of the film itself falls, and it has become the cause of delaying utilization of a super-water repellent film.
[0007]this invention is made in view of such a problem, and comes out. ** is easy for the purpose and it is in providing the paint used for a membrane structure object which combines the outstanding hardness and planing nature simultaneously, a manufacturing method for the same, and the manufacturing method concerned.

[0008]
[Means for Solving the Problem]In order to attain the above purposes, in this invention, a foundation layer of minute porosity which has much micropores of 100 nm - 2 micrometers of average pore sizes is formed using phase splitting, and a high hardness quantity planing nature film is produced by giving a water-repellent finish at this foundation layer.
[0009]The 1st rugged surface in which the surface of a substrate was formed in the 1st surface roughness in this invention in order to improve super-water repellence further, It is formed in a field which has double surface roughness with the 2nd rugged surface formed on the 1st rugged surface in the 2nd surface roughness smaller than the 1st surface roughness, and a high hardness quantity planing nature film is produced by giving a water-repellent finish at this foundation layer. while forming the 1st rugged surface in formation of a field of this double surface roughness using the same phase splitting as the above -- a pan -- the 2nd rugged surface can be formed using phase splitting of a fine diameter of distribution, or particles.
[0010]As a manufacturing method of a high hardness quantity planing nature film which fills such a demand, For example, a metal alkoxide and/or sol with a primary particle diameter of 100 nm or less, Carry out phase splitting to these in a solvent, and it decomposes at temperature from a room temperature to 700 **, After a substance which has the characteristic burned and sublimated produces a solution or an emulsion added by solvent and produces a film at ordinary temperature (room temperature) using this, fixed time maintenance can be carried out at temperature from a room temperature to 700 **, and a method of removing the above-mentioned substance can be mentioned. It is possible to fill the above-mentioned demand also with combination of particles from which a size (particle diameter) differs, or diameter control of condensation of particles.
[0011]The water-repellent finish can use what combined suitably fluoride, water repellent

of a silicone series, or these. In order to give self cleaning nature to a high hardness quantity planing nature film concerning this invention, it is possible to also make a foundation layer of said porosity contain a photocatalyst.
[0012]More specifically, this invention provides the following.
[0013](1) A high hardness quantity planing nature film having practical hardness and high planing nature.
[0014](2) A high hardness quantity planing nature film provided with the following characteristic.
A fall angle of a drop whose angles of contact are not less than 140 degrees and 7 mg is 30 degrees or less, and hardness is more than 3H at pencil hardness. Speaking of a fall angle, 20 degrees or less are 15 degrees or less more preferably. Speaking of hardness, more than 5H is more than 6H in pencil hardness more preferably at pencil hardness. About such fall angles and hardness, it can attain by each applying this invention.
[0015](3) (1) which is the high planing nature film provided with a minute porous layer which equips the surface with much micropores of 100 nm - 2 micrometers of average pore sizes, or a high hardness quantity planing nature film given in (2).
[0016](4) A high hardness quantity planing nature film in which a water-repellent finish was given to the surface and which consists of a minute porous layer provided with much micropores which are 100 nm - 2 micrometers of average pore sizes.
[0017](5) A high hardness quantity planing nature film given in either of (1) to (4) which is a transparent membrane.
[0018](6) A high hardness quantity planing nature film characterized by foundation layer which has fine pores of 100 nm - 2 micrometers of average pore sizes formed using phase splitting, and the porous thing of the surface for which a transparent hydrophobic layer is formed in part at least.
[0019](7) A high hardness quantity planing nature film, wherein the surface is formed in a field which has the double surface roughness of the 1st rugged surface formed in the 1st surface roughness, and the 2nd rugged surface formed on the 1st rugged surface in the 2nd surface roughness smaller than the 1st surface roughness.
[0020](8) A high hardness quantity planing nature film given in (7) whose 2nd surface roughness the 1st surface roughness is in a range which are 100 nm - 2 micrometers, and is less than 100 nm. A field of making air placed between crevices by this surface roughness, and raising super-water repellence more although a lower limit in particular of the 2nd surface roughness does not limit, And from a field of forming the 2nd surface roughness practical using phase splitting or particle content, about 1 nm of lower limits of the 2nd surface roughness are about 3 nm more preferably.
[0021](9) (7) in which the 1st rugged surface is formed in using phase splitting, and the 2nd rugged surface is formed using phase splitting or content particles, or a high hardness quantity planing nature film given in (8).
[0022](10) (7) in which the 1st rugged surface is formed in using particles or floc of bigger particle diameter, and the 2nd rugged surface is formed using particles or a primary particle of smaller particle diameter, or a high hardness quantity planing nature film given in (8).
[0023](11) A high hardness quantity planing nature film given in either of (7) to (10) which is a transparent membrane.
[0024](12) A high hardness quantity planing nature film given in surface either of (7) to

(11) in which a hydrophobic layer is formed in part at least.
[0025](13) A high hardness quantity planing nature film given in either of (1) to (12) by which a photocatalyst is distributed.
[0026]Thus, what a photocatalyst (typically titanium oxide) is distributed for (a foundation layer of minute porosity is distributed suitably) can give self cleaning nature (Japanese Patent Application No. No. 294637 [11 to]) to a high hardness quantity planing nature film of this invention.
[0027](14) An undiluted solution of paint for high hardness quantity planing nature film formation which consists of a thing in which phase splitting was formed, by a substance removed after raw material liquid of a film substrate, a predetermined solvent, and raw material liquid of said film substrate solidify.
[0028]In this invention, paint for high hardness quantity planing nature film formation is produced by dissolving this undiluted solution in a predetermined solvent (an example of a concrete mode is shown in following (15) - (18)). As long as it can give practical hardness to a planing nature film obtained eventually [here / "raw material liquid of a film substrate" is what can form phase splitting among other ingredients, and], it may be what kind of thing, and as an example, a metal alkoxide used as a raw material of a sol-gel method is mentioned. A substance (substance which has the characteristic especially burned [which burn and is decomposed] and sublimated at temperature from a room temperature to 700 **) which has the characteristic removed at temperature from a room temperature to 700 ** as "a substance removed after raw material liquid of a film substrate solidifies" can be mentioned as an example.
[0029](15) Paint for high hardness quantity planing nature film formation in which a substance which has the characteristic which carries out phase splitting to the metal alkoxide concerned a metal alkoxide and in a predetermined solvent, and is removed from a room temperature at temperature up to 700 **, and ** consist of a solution or an emulsion added by solvent.
[0030](16) Paint for high hardness quantity planing nature film formation in which a substance which has the characteristic which carries out phase splitting to these a metal alkoxide, sol with a primary particle diameter of 100 nm or less, and in a predetermined solvent, and is removed from a room temperature at temperature up to 700 **, and ** consist of a solution or an emulsion added by solvent.
[0031]"The characteristic removed at temperature from a room temperature to 700 **", For example, the characteristic decomposed, burned and sublimated at this temperature will be meant, and what can form phase splitting among other ingredients will be suitably chosen out of a substance group (for example, a group of a heat sublimability substance) provided with such the characteristic. As such a thing, it is organic polymer (generally this decomposes and burns with heat), and it is insoluble to a metal alkoxide and what is dissolved in predetermined solvents, such as ethanol and ethyl acetate, can be mentioned.
[0032](17) said sol -- colloidal silica -- paint for high hardness quantity planing nature film formation given in (16) which consists of sol.
[0033]A diameter of distribution in a phase-splitting state which it has the characteristic which carries out phase splitting to a metal alkoxide with this in a predetermined solvent, and is removed from a room temperature at temperature up to 700 ** (18) A not less than 100-nm substance and a substance below 100 nm, Paint for high hardness quantity planing nature film formation which consists of a solution or an emulsion added by

******.
[0034]After applying paint of someday a statement of (19) and (15) to (18) to a substrate, How to form a foundation layer of minute porosity and form a high hardness quantity planing nature film on said substrate by applying water repellent to at least a part of this foundation layer by heat-treating in a temperature requirement from a room temperature to 700 **.
[0035]In this invention, it is also still more possible to apply paint containing particles of a different size as follows and a method of forming a high hardness quantity planing nature film using the paint.
[0036](20) Paint for high hardness quantity planing nature film formation in which particle diameter contains particles or a primary particle below 100 nm with a not less than 100-nm particle or floc in particle diameter.
[0037](21) The 1st rugged surface that applied paint given in the above (20) to a substrate, in which particle diameter was formed of particles or floc not less than 100-nm and that was formed in the 1st surface roughness, Particle diameter forms a foundation layer with a field which has double surface roughness with the 2nd rugged surface where it was formed on the 1st rugged surface in the 2nd surface roughness smaller than the 1st surface roughness formed of particles or a primary particle below 100 nm, How to form a high hardness quantity planing nature film on a substrate by applying water repellent to at least a part of this foundation layer.
[0038]Furthermore in this invention, following methods are employable.
(22) How to produce a high planing nature film by giving a water-repellent finish on the surface of a minute porous layer provided with much micropores of 100 nm - 2 micrometers of average pore sizes.
[0039](23) How to produce a high planing nature film by giving a water-repellent finish in a base material surface which has the double surface roughness of the 1st rugged surface that has the 1st surface roughness, and the 2nd rugged surface formed on the 1st rugged surface by the 2nd surface roughness smaller than the 1st surface roughness.
[0040](24) A method given in (23) whose 1st rugged surface is 100 nm - 2 micrometers of surface roughness and whose 2nd rugged surface is less than 100 nm of surface roughness.
[0041]How applying water repellent of a fluorine system to either of (25) and (19) to (24) in a method of a statement.
[0042]How to perform adjustment of planing nature intensity of a planing nature film and/or adjustment of hardness which are eventually obtained by performing adjustment of a state of said phase splitting, and/or adjustment of a heat treatment process to either of (26) and (15) to (18) using paint of a statement.
[0043]
[Embodiment of the Invention]In order to make an understanding of this invention easy, an embodiment is described concretely and in detail. It is desirable to make small the difference of the advance contact angle (angle of contact by the side of advance of a drop) and reducing contact angle (angle of contact by the side of retreat of a drop) at the time of a drop falling the sloping field, in order to obtain good planing nature, For that purpose, fixed granularity is given to a film, The field is ******(ed). Contribution by bite lump of air. Making [many] it. [effective] Johnson Jr., R.E. & Dettre, R. H. Contact Angle Hysteresis, I. Studyof an Ideal Rough Surface,Adv. Chem. Ser. and 43. 112-135

(1963),
[0044]In order to obtain good planing nature, it is specifically most desirable to make a surface structure needlelike, but with such a structure, surface hardness is unmaintainable. In order to give the hardness which this invention persons can maintain planing nature and water repellence, and can be used for a film in view of such a thing, As a result of examining the structure of a membrane surface wholeheartedly, the substance which has the characteristic which carries out phase splitting to a metal alkoxide and/or sol with a primary particle diameter of 100 nm or less with these in a solvent, and is burned [which burn and is decomposed] and sublimated at the temperature from a room temperature to 700 ** produced the solution or emulsion added by the solvent. And by carrying out fixed time maintenance at the temperature from a room temperature to 700 **, after producing a film at ordinary temperature using this, It found out that the film outstanding in respect of hardness and planing nature was producible by forming the structure of minute porosity of having much micropores of 100 nm - 2 micrometers of average pore sizes accompanying phase separation, and giving a water-repellent finish at this.
[0045]Since the film obtained by this invention is a film of minute porosity, it has obtained high hardness, without spoiling planing nature and water repellence. As long as a membranous construct fulfills a size and soluble conditions, is clear and is, it may combine two or more substances.
[0046]Although the construction material of a film usable with this invention is mainly an inorganic material, they may be organic materials as long as it has suitable hardness and heat resistance. Membranous manufacturing methods are mainly wet process, such as a spin coat, dip coating, and a spray method. the substance burned [which burn and is disassembled] and sublimated at the temperature from a room temperature to 700 ** is also boiled as it is an organic matter as it is an inorganic substance, and it is not limited.
[0047]In this invention, while forming the 1st rugged surface on the surface of a substrate, for example with the same porous-layer formation method as the above, the field which has the double surface roughness in which the 2nd still finer rugged surface was formed on the 1st rugged surface can also be formed. It becomes possible to attain high surface hardness simultaneously, forming a still finer air intervening layer and improving water repellence further by this structure. As a method of attaining the 2nd surface roughness that forms the 2nd rugged surface, Decomposition, combustion, and sublimation remove the method of forming by containing particles, such as colloidal silica, and the substance which carried out phase splitting with the diameter of distribution still finer than the above-mentioned phase splitting, and the method of a top carrying finer porous structure and having it, etc. can be adopted.
[0048][Water repellent] Although it is possible as water repellent to use the water repellents or such combination of fluoride or a silicone series, since the effect that the thing containing fluoride reduces surface energy is large, it is desirable, and especially a fluoro alkyl silane is preferred. In addition, a perfluoroalkyl carboxylic acid system, a perfluoroalkyl sulfonic acid system, It is usable in various fluororesin and fluoridation graphite, a fluoridation pitch, etc. which are represented by finishing agents, such as a perfluoro alkyl-phosphoric-acid system, perfluoroalkyl group content oligomer, and polytetrafluoroethylene (PTFE).
[0049]Like the foundation layer of minute porosity, although wet process is most excellent in respect of efficiency or cost, depending on a raw material, it may be made to

perform a water-repellent finish by vacuum deposition or a sputtering technique.
[0050][Photocatalyst] As a photocatalyst material which can be added, it can be used combining one kind or plurality among titanium oxide, tin oxide, a zinc oxide, strontium titanate, tungstic oxide, iron oxide, and copper oxide. Various kinds of inorganic matter which produces these photocatalysts with heating as these precursors, An organic compound is mentioned, for example, when it is titanium oxide, titanium alkoxides, such as titanium hydroxide and titanium tetrapropoxide. A titanium chloride, a titanium sulfide, titanium bromide, titanium iodide, bis(cyclopentadienyl) titanium, Dicarbonyl bis(cyclopentadienyl) titanium, chloro bis(cyclopentadienyl) titanium, dichlorobis cyclopentadienyl titanium, dimethyl bis(cyclopentadienyl) titanium, trichloro cyclopentadienyl titanium, tetrabenzyltitanium, etc. are mentioned.
[0051]Since it has here the character which disassembles organic water repellent, for example about a titanium oxide photocatalyst although two or more substances may be combined if the membranous construct fulfills a size and soluble conditions, In putting a titanium oxide photocatalyst into a film, adjust the concentration to about 2wt%, or (about this, verified in a next example). Or it is desirable to constitute a substrate from an oxide, hydroxide, or those mixtures, such as silicon, aluminum, and a zirconium, and to add a titanium oxide photocatalyst in the quantity of the range of 0.5 - 60wt% of these substrates. If the addition of a photocatalyst increases more than this, photocatalyst activity will increase, but in order for the endurance of water repellent to fall, an angle of contact will fall for a short time.
[0052][Planing nature] The super-water repellence surface can make the touch area of the surface and water remarkably small. Although static water repellence is estimated by the angle of contact, the dynamic water repellence, i.e., planing nature, is more important practically. This is estimated by the difference (hysteresis) of the angle (fall angle) at which a drop starts a fall when a flat field is leaned, the drop in that case and the advance contact angle which a field builds, and a reducing contact angle, and the tendency which attaches greater importance than to an angle of contact to these indices is strong in recent years. It does not necessarily restrict that the fall angle of the drop of a solid surface with a high angle of contact is always low, but although an angle of contact is high, it may show a high fall angle. [it] [it] For example, if smooth glass is coated with FAS-17 ($CF_3(CF_2)_7CH_2CH_2Si(OMe)_3$), although the fall angle in a drop (about 105 degrees and 20 mg) is about 50 degrees, a water contact angle, With the glass which carried out the coat of the methyl trimetoxysilane, although a water contact angle is as low as about 64 degrees, the fall angle of a 20-mg drop becomes lower than FAS-17 at about 35 degrees.
[0053][Use] Although what has a film having practical hardness and the outstanding planing nature suitable until now was not obtained, such a film is provided by this invention.
[0054]The film having the practical hardness concerning this invention, and the outstanding planing nature, The exterior, the ship bottom paint, the outdoor light, the kitchen, and kitchen utensils of vehicles, such as a car and the Shinkansen, The floor and the exterior of a bathroom, a washroom, and the article, the net for fishings, a buoy, dental supply, an electric appliance and a residence, A front door and a knob, a roof, a pool and the poolside, a bridge pier, a gate, a mailbox, A bench, a steel tower, an antenna, an electric wire, a garage, tentorium, an umbrella, a raincoat, Leather articles, such as sporting goods and sport garments, a helmet, shoes, and a bag, Chemical processing

plants, such as lubricating nozzles, such as outdoor speakers and audio equipment, such as a camera, video, paper, and a speaker, a curtain, a carpet, and a gas station, and an oil refinery, metal tools, a nail, a screw and buckets, etc. can consider far-reaching application.

[0055]

[Example]Hereafter, the example of this invention is shown.

[0056]This example adjusted a solvent, a metal alkoxide, and the concentration of three ingredients of polymer, and formed phase splitting according to the scheme shown in drawing 2 so that it might enter within phase splitting in the phase diagram of three component systems shown in drawing 1. Obtained phase splitting is a heterogeneous system, and as shown in drawing 3, it is considered that what the fine grain of polymer distributed was formed into what alcohol (solvent) and an alkoxide dissolved mutually. silica -- it is thought that the silica particle (for example, colloidal silica) in which sol was formed was distributing.

[0057]As a result of giving a water-repellent finish by performing solidification of the paint concerned, and removal of polymer by heat-treating the paint in the above phase-splitting states, the surface (surface of minute porosity) where much micropores as shown in drawing 4 exist was obtained (SEM photograph). The section of this micropore is considered that the base material surface 2 which has the crater-like micropore 1 as shown in drawing 5 was formed.

[0058]although only unevenness of the base material surface by the micropore 1 of the shape of an above crater can acquire super-water repellence -- silica -- by adding sol and making particles, such as colloidal silica, contain, on the above-mentioned surface unevenness, a top can carry still minuter unevenness and it can be carried out. This further fine-irregularities formation can be formed using phase splitting, compared with dispersing polymer for concavo-convex crater formation of the above, makes the quality of a split-phase type product of the still finer diameter of distribution contain, and can be formed also by removing it by heat treatment.

[0059]That is, as a model figure is shown in drawing 6, when only the 1st rugged surface 11 by the micropore of the shape of a crater which was mentioned above, for example is formed in the surface of the substrate 10, although the slant face 12 in each uneven part of the turns into a comparatively flat field, it presents the water repellence outstanding to the drop 13.

[0060]On the other hand, if the 2nd fine rugged surface 22 is formed in the surface of the substrate 20 by an it top in addition to the 1st rugged surface 21 by the micropore of the shape of a crater which was mentioned above, for example as a model figure is shown in drawing 7, the water repellence further outstanding to the drop 23 can be demonstrated.

[0061]20 g of example 1 ethanol, 2 g of tetraethyl orthosilicate (TEOS), and the chloride 1.2g were mixed for 36 hours, and it hydrolyzed. On the other hand, acrylic polymer was dissolved in ethanol and it adjusted to 5.4% of solid content. And after adding 4g of this acrylic polymer / ethanol solution in the solution of TEOS and also adding 4g of ethanol, coating liquid was prepared by 0.12g of silica sol (colloidal silica) adding to this. This coating liquid formed phase splitting which acrylic polymer distributed into the hydrolysis TEOS ethanol solution.

[0062]After carrying out the spin coat of this phase-splitting coating liquid by 1500 rotations on Pyrex (registered trademark) glass and repeating the cycle of coat desiccation

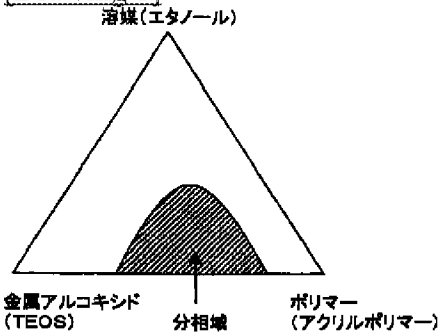
10 times, it calcinated at 500 ** for 30 minutes. Thus, it gave a water-repellent finish by carrying out the coat of the fluoro alkyl silane hydrolyzed with the water of the equivalent to the obtained film with a heat CVD method, and the planing nature film was produced.
[0063]The obtained planing nature film has the minute porous structure of the shape of a crater of 1 micrometer of average pore sizes.
Furthermore it was furthermore based on colloidal silica on it, fine fine irregularities were formed, it was 157 degrees and the angle of contact was a high hardness quantity planing nature film in which the fall angle of a 7-mg drop is provided with the hardness of 8H with 6.5 degrees and pencil hardness.

[0064]After applying the sol which distributed nitric acid content boehmite 0.24wt% to the ethanol solution (2.37wt%) of comparative example 1 acetylacetone aluminum on Pyrex glass in a spin coat, The cycle of calcinating for 20 seconds on a 500 ** hot plate was repeated 5 times, and the transparent membrane was produced. After dipping for 40 minutes in the 2% methanol solution of the fluoro alkyl silane which hydrolyzed this transparent membrane with the water of the equivalent, it gave a water-repellent finish by having dried for 20 minutes at 140 **, and the planing nature film was obtained.
[0065]Although the obtained planing nature film had the minute porous structure of 200 nm of average pore sizes and the angle of contact was 155 **, the fall angle of a 7-mg drop is about 30 degrees.
The hardness was 3B in pencil hardness.

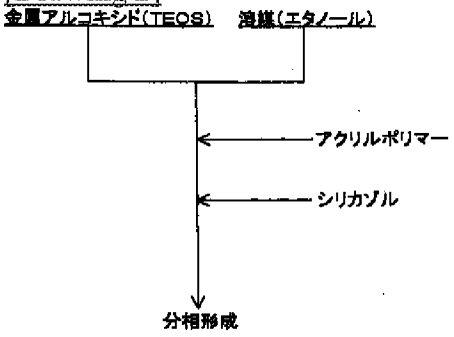
[0066]The paint of the same presentation as the paint concerning the above-mentioned Example 1 was prepared independently, and membrane formation and a water-repellent finish were performed [except / of having prepared without adding comparative example 2 acrylic polymer] by the same method as the above-mentioned example.
[0067]Although the obtained film was precise transparence, hardness was as high as 8H at pencil hardness and the angle of contact was 133 degrees, even if it leaned the film to 90 degrees, a 7-mg drop did not fall and planing nature had not revealed it.
[0068]example 2 ethanol: -- the silica of marketing which mixes 10 g, dark HCl:0.6g, and tetraethyl orthosilicate:1.0g for 19 hours, and shows compatibility at this to methyl ethyl ketone (MEK) -- sol (particle diameter: 15 nm) was added, and the spin coat was performed at 1500 rpm. When it gave a water-repellent finish by the same method as Example 1 with the heat CVD at this, the high hardness super-water-repellent membrane of the angle of contact of 152 degrees of water, the fall angle of 30 degrees of a 7-mg drop, and the pencil hardness 3H was obtained. this film -- silica with a primary particle diameter of 15 nm -- sol had become the double granularity structure which formed the crumb structure which is 600 nm in 2nd order. A SEM photograph is shown in drawing 8.
[0069]the MEK system silica of comparative example 3 Example 2 -- the alcohol system silica which was excellent in the dispersibility in the inside of ethanol instead of sol -- sol (particle diameter: 15 nm) was used. As a result, even if the angle of contact leaned 90 degrees of 7-mg drops by 131-degree ******, it did not fall.
[0070]
[Effect of the Invention]As explained above, according to this invention, the high hardness quantity planing nature film of the controlled structure is easily producible. It is

suitably [for various kinds of industrial commodities] usable, and this contributes to a wide range use.

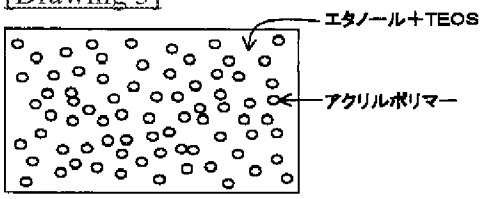
[Drawing 1]



[Drawing 2]

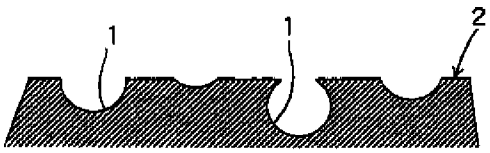


[Drawing 3]

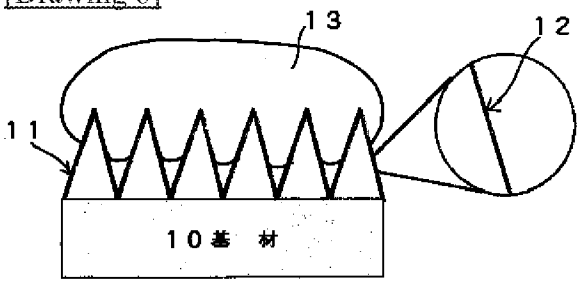


[Drawing 4]

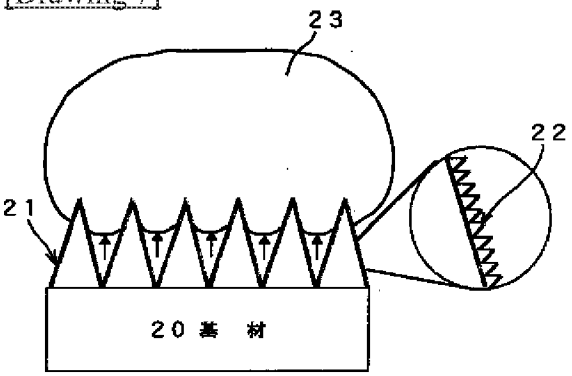
[Drawing 5]



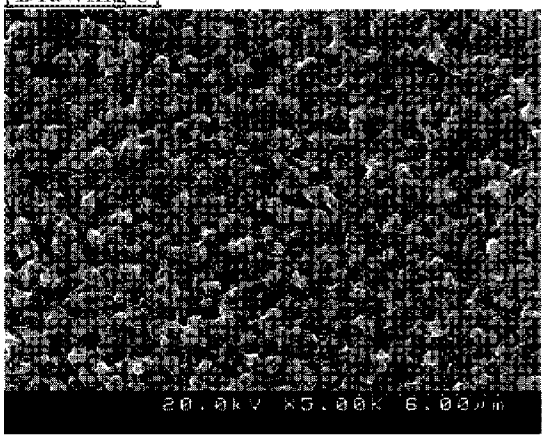
[Drawing 6]



[Drawing 7]



[Drawing 8]



CLAIMS

[Claim(s)]

[Claim 1]A high hardness quantity planing nature film having practical hardness and high planing nature.

[Claim 2]A high hardness quantity planing nature film provided with the following characteristics. A fall angle of a drop whose angles of contact are not less than 140

degrees and 7 mg is 30 degrees or less, and hardness is more than 3H at pencil hardness.
[Claim 3]The high hardness quantity planing nature film according to claim 1 or 2 which is a high planing nature film provided with a minute porous layer which equips the surface with much micropores of 100 nm - 2 micrometers of average pore sizes.
[Claim 4]A high hardness quantity planing nature film in which a water-repellent finish was given to the surface and which consists of a minute porous layer provided with much micropores which are 100 nm - 2 micrometers of average pore sizes.
[Claim 5]The high hardness quantity planing nature film according to any one of claims 1 to 4 which is a transparent membrane.
[Claim 6]A high hardness quantity planing nature film characterized by foundation layer which has fine pores of 100 nm - 2 micrometers of average pore sizes formed using phase splitting, and the porous thing of the surface for which a transparent hydrophobic layer is formed in part at least.
[Claim 7]A high hardness quantity planing nature film currently forming in a field characterized by comprising the following.
The 1st rugged surface in which the surface was formed in the 1st surface roughness.
Double surface roughness with the 2nd rugged surface formed on the 1st rugged surface in the 2nd surface roughness smaller than the 1st surface roughness.

[Claim 8]The high hardness quantity planing nature film according to claim 7 whose 2nd surface roughness the 1st surface roughness is in a range which are 100 nm - 2 micrometers, and is less than 100 nm.
[Claim 9]The high hardness quantity planing nature film according to claim 7 or 8 in which the 1st rugged surface is formed using phase splitting, and the 2nd rugged surface is formed using phase splitting or content particles.
[Claim 10]The high hardness quantity planing nature film according to claim 7 or 8 in which the 1st rugged surface is formed using particles or floc of bigger particle diameter, and the 2nd rugged surface is formed using particles or a primary particle of smaller particle diameter.
[Claim 11]The high hardness quantity planing nature film according to any one of claims 7 to 10 which is a transparent membrane.
[Claim 12]The surface high hardness quantity planing nature film according to any one of claims 7 to 11 in which a hydrophobic layer is formed in part at least.
[Claim 13]The high hardness quantity planing nature film according to any one of claims 1 to 12 in which a photocatalyst is distributed.
[Claim 14]An undiluted solution of paint for high hardness quantity planing nature film formation which consists of a thing in which phase splitting was formed, by a substance removed after raw material liquid of a film substrate, a predetermined solvent, and raw material liquid of said film substrate solidify.
[Claim 15]Paint for high hardness quantity planing nature film formation in which a substance which has the characteristic which carries out phase splitting to the metal alkoxide concerned a metal alkoxide and in a predetermined solvent, and is removed from a room temperature at temperature up to 700 **, and ** consist of a solution or an emulsion added by solvent.
[Claim 16]Paint for high hardness quantity planing nature film formation in which a substance which has the characteristic which carries out phase splitting to these a metal

alkoxide, sol with a primary particle diameter of 100 nm or less, and in a predetermined solvent, and is removed from a room temperature at temperature up to 700 **, and ** consist of a solution or an emulsion added by solvent.
[Claim 17]said sol -- colloidal silica -- paint for the high hardness quantity planing nature film formation according to claim 16 which consists of sol.
[Claim 18]A diameter of distribution in a phase-splitting state which it has the characteristic which carries out phase splitting to a metal alkoxide with this in a predetermined solvent, and is removed from a room temperature at temperature up to 700 ** A not less than 100-nm substance and a substance below 100 nm, Paint for high hardness quantity planing nature film formation which consists of a solution or an emulsion added by ******.
[Claim 19]How to form a foundation layer of minute porosity and form a high hardness quantity planing nature film on a substrate by applying water repellent to at least a part of this foundation layer by heat-treating in a temperature requirement from a room temperature to 700 **, after applying the paint according to any one of claims 15 to 18 to a substrate.
[Claim 20]Paint characterized by comprising the following for high hardness quantity planing nature film formation.
Particle diameter is particles or floc not less than 100-nm.
Particle diameter is particles or a primary particle below 100 nm.

[Claim 21]How to form a foundation layer with a field characterized by comprising the following, and form a high hardness quantity planing nature film on a substrate by applying water repellent to at least a part of this foundation layer.
The 1st rugged surface that applied the paint according to claim 20 to a substrate, in which particle diameter was formed of particles or floc not less than 100-nm and that was formed in the 1st surface roughness.
Double surface roughness with the 2nd rugged surface formed on the 1st rugged surface in the 2nd surface roughness whose particle diameter is smaller than the 1st surface roughness formed of particles or a primary particle below 100 nm.

[Claim 22]How to produce a high planing nature film by giving a water-repellent finish on the surface of a minute porous layer provided with much micropores of 100 nm - 2 micrometers of average pore sizes.
[Claim 23]How to produce a high planing nature film by giving a water-repellent finish in a base material surface characterized by comprising the following.
The 1st rugged surface that has the 1st surface roughness.
Double surface roughness with the 2nd rugged surface formed on the 1st rugged surface by the 2nd surface roughness smaller than the 1st surface roughness.

[Claim 24]A way according to claim 23 the 1st rugged surface is in a range which is 100 nm - 2 micrometers of surface roughness, and the 2nd rugged surface is less than 100 nm of surface roughness.
[Claim 25]How applying water repellent of a fluorine system in a method according to any one of claims 19 to 24.
[Claim 26]How to perform adjustment of planing nature intensity of a planing nature film

and/or adjustment of hardness which are eventually obtained using the paint according to any one of claims 15 to 18 by performing adjustment of a state of said phase splitting, and/or adjustment of a heat treatment process.